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A - [001] 017 04- 143 311 431 443 445 477 540 57& 575 596 604 608
- [002] 017 04- 150 431 443 445 477 540 57& 609
- [003] 017 034 04- 041 046 431 435 443 477 502 540 57& 575 596 688
- [004] 017 04- 143 144 166 171 431 435 445 472 477 494 540 57& 575 596
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DC - A32 A94
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IN - KANO M; SASAKI N; SEKIGUCHI M
KS - 0222 0231 0232 0233 1288 1294 2419 2499 2513 2522 2547 2654 2667 2680
2682 2726 2729 3178 3255
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MC - A04-G01E A05-E01D A05-E04E A11-B09D A12-S06C A12-S07A
PA - (TOPP) TOPPAN PRINTING CO LTD
PN - JP5269914 A 19931019 DW199346
JP2760203B2 B2 19980528 DW199826
PR - JP19920070849 19920327
XIC - B32B-027/36; B32B-027/40; B32B-007/02; B32B-007/12; B32B-009/00
AB - The laminated sheet is prepd. by laminating (A) thin metal oxide film
having a thickness of 450-1,500 Angstroms, (B) transparent primer
layer consisting of resin having a glass transition point of above 40
deg.C, pref. 40-80 deg.C, (C) two-pack type urethane adhesive layer
and (D) polyolefin resin layer on (E) transparent plastic film. A
printing layer (F) is formed between (B) and (C).
(E) has a thickness of 3-200, pref. 6-100 microns and pref. is
biaxially oriented polyethylene terephthalate film. Pref. metal oxide
is magnesium oxide. (B) has a thickness of 0.5-3 microns. Pref. is
polyester resin primer. (D) has a thickness of 15-120 microns.
- ADVANTAGE :
The laminated sheet has high transparency and excellent oxygen and
water vapour barrier property.
ICAI- B32B27/36; B32B27/40; B32B7/02; B32B7/12; B32B9/00
ICCI- B32B27/36; B32B27/40; B32B7/02; B32B7/12; B32B9/00
INW - KANO M; SASAKI N; SEKIGUCHI M
IW - HIGH TRANSPARENT LAMINATE SHEET PREPARATION THIN METAL OXIDE FILM
PRIME LAYER POLYURETHANE ADHESIVE POLYOLEFIN RESIN
IWW - HIGH TRANSPARENT LAMINATE SHEET PREPARATION THIN METAL OXIDE FILM
PRIME LAYER POLYURETHANE ADHESIVE POLYOLEFIN RESIN
NC - 1
NPN - 2
OPD - 1992-03-27
PAW - (TOPP) TOPPAN PRINTING CO LTD
PD - 1993-10-19
TI - High transparency laminated sheet - prepd. by laminating thin metal
oxide film, transparent primer layer, urethane! adhesive layer and
polyolefin resin layer
A01 - [001] 017; P0839-R F41
- [002] 017; ND01; Q9999 Q7818-R; Q9999 Q6780; K9701 K9676; B9999 B4397
B4240; N9999 N7192 N7023; B9999 B4864 B4853 B4740

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- [003] 017; Q9999 Q7192 Q7114; B9999 B5243-R B4740; B9999 B5618 B5572;
  K9610 K9483; K9574 K9483; B9999 B5447 B5414 B5403 B5276; B9999 B5414-R
  B5403 B5276
A02 - [001] 017; P1592-R F77
- [002] 017; ND01; Q9999 Q7818-R; Q9999 Q6780; K9701 K9676; B9999 B4397
  B4240; N9999 N7192 N7023; B9999 B4864 B4853 B4740
- [003] 017; Q9999 Q6644-R; K9574 K9483; K9610 K9483
A03 - [001] 017; G0033-R G0022 D01 D02 D51 D53; H0000; H0011-R; S9999 S1581;
  S9999 S1285-R; P1150
- [002] 017; ND01; Q9999 Q7818-R; Q9999 Q6780; K9701 K9676; B9999 B4397
  B4240; N9999 N7192 N7023; B9999 B4864 B4853 B4740
- [003] 017; K9574 K9483; B9999 B5243-R B4740; K9712 K9676
A04 - [001] 017; P0884 P0839 H0293 F41; S9999 S1285-R
- [002] 017; ND01; Q9999 Q7818-R; Q9999 Q6780; K9701 K9676; B9999 B4397
  B4240; N9999 N7192 N7023; B9999 B4864 B4853 B4740
- [003] 017; B9999 B5243-R B4740; B9999 B5163 B5152 B4740; K9610 K9483;
  B9999 B5436 B5414 B5403 B5276

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PATENT ABSTRACTS OF JAPAN

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(21)Application number : **04-070849**

(71)Applicant : **TOPPAN PRINTING CO LTD**

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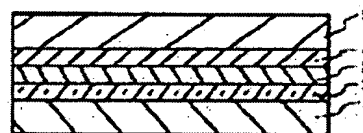
(72)Inventor : **SEKIGUCHI MAMORU
SASAKI NOBORU
KANO MITSURU**

(54) **LAMINATE**

(57)Abstract:

PURPOSE: To solve such a problem that oxygen barrier properties are deteriorated by forming a laminate using a film having a metal oxide membrane formed thereto.

CONSTITUTION: A metal oxide membrane 2 with a thickness of 450-1500 μ m; composed of magnesium oxide, a transparent primer layer 3 composed of a resin with a glass transition point of 40°C or higher, a two-pack type urethane adhesive layer 4 and a polyolefin resin layer 5 are successively laminated on a transparent plastic film 1.



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CLAIMS

[Claim(s)]

[Claim 1]A layered product laminating a transparent primer layer, a 2 liquid hardening type urethane system adhesives layer, and a polyolefin resin layer which consist of a metal oxide thin film (450A - 1500 A) and resin of not less than 40 ** of glass transition points on a transparent plastic film one by one.

[Claim 2]The layered product according to claim 1 providing a printing layer further between a transparent primer layer and a 2 liquid hardening type urethane system adhesives layer.

[Claim 3]Claim 1, wherein a metal oxide thin film is a magnesium oxide thin film, a layered product of two descriptions.

[Claim 4]The layered product according to claim 1 to 3, wherein a transparent primer layer is the thickness which is 0.5-3 micrometers.

[Claim 5]The layered product according to claim 1 to 4, wherein a transparent primer layer is polyester resin.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the outstanding barrier property layered product to oxygen and a steam especially with transparency with respect to the layered product which has metal oxide thin films, such as magnesium oxide.

[0002]

[Description of the Prior Art]It is publicly known that gas cutoff nature, such as oxygen and a steam, can be given by forming metal oxide thin films, such as oxidized silicon and an aluminum oxide, by methods, such as a vacuum deposition method and sputtering, on a high polymer film (U. S.Pat.3,442,686, JP,S63-28017,B, etc.). The deposition film obtained by this is being put in part in practical use by metal deposition by the wrapping of the oxygen interception nature which has transparency which is not obtained taking advantage of the feature of a metallic oxide.

[0003]However, the oxygen interception nature of the various deposition film including an oxidized silicon system itself, Although the thing stable to some extent came to be obtained, when putting in practical use, It is required to extrude the thermoplastic polymer resin of the dry laminate method, the non solvent laminating method, and a molten state which pastes adhesives together to a substrate besides after coating from a T die etc., and to obtain a layered product by publicly known methods, such as an EKUSUTO Roussillon lamination which forms membranes.

[0004]In order to obtain the gas (oxygen, steam) interception nature stable in the form of such a layered product, it is required to prevent degradation of the thin film by the tension which a deposition film receives at the time of lamination, the no produced by the difference in the thermal expansion of a substrate and a metallic oxide, etc.

[0005]The deterioration degree after lamination of the above-mentioned gas cutoff nature layered product changes with the kind of metallic oxide, the kind of layered product style material, laminating methods, etc. It had left the problem to the composition and the processing method which have the gas cutoff nature stable in the form of the layered product as mentioned above.

[0006]

[Problem(s) to be Solved by the Invention]Like the above, there was a problem that oxygen interception nature deteriorated, by making a metallic-oxide deposition film into a layered product with a publicly known laminating method.

[0007]Then, an object of this invention is to provide the layered product using a metallic-oxide film without degradation of gas cutoff nature, especially a magnesium oxide system deposition film.

[0008]

[Means for Solving the Problem]In order to attain this purpose, a layered product laminating a transparent primer layer, a 2 liquid hardening type urethane system adhesives layer, and a polyolefin resin layer which consist of a metal oxide thin film (450A - 1500 A) and resin of not less than 40 ** of glass transition points on a transparent plastic film one by one is provided.

[0009]It is also included that a layered product provided a printing layer further between a transparent primer layer and a 2 liquid hardening type urethane system adhesives layer, that a metal oxide thin film is a magnesium oxide thin film, that a transparent primer layer is the thickness which is 0.5-3 micrometers, and that a transparent primer layer is polyester resin.

[0010]This invention is explained in detail using Drawings. Drawing 1 and drawing 2 are the sectional views of a layered product concerning this invention.

[0011]The transparent plastic film 1 used for this invention, If used as a base material of a metal oxide thin film, there will be no restriction in particular, but. Preferably Polyolefine; polyethylene terephthalate, such as polyethylene and polypropylene, Polybutylene terephthalate, Polyester [, such as polyethylenenaphthalate,];. Polyamide; polycarbonate; polystyrene; polyvinyl chloride; polyimide; polyether imide; polyphenylene sulfides, such as nylon 6 and Nylon 12; Synthetic macromolecule films, such as polyvinyl fluoride, etc. are used, A polyethylene terephthalate film extended arbitrarily is preferably used especially for 2 shaft orientations.

[0012]Publicly known various additive agents, stabilizer, for example, a spray for preventing static electricity, an ultraviolet ray absorbent, a plasticizer, lubricant, etc. can be included in the above-mentioned plastic film.

[0013]Practical, a range of thickness of the above-mentioned plastic film is 3-200 micrometers, and its 6-100 micrometers are preferred according to a use.

[0014]Metal oxide thin films concerning this invention are oxides, such as magnesium; aluminum; titanium; zinc; cobalt; nickel; tin; zirconium; silicon, Especially if it has transparency and has gas (oxygen, steam) interception nature, it is not limited, but a magnesium oxide thin film in which barrier property which was [as opposed to / especially / a steam] excellent is shown is preferred.

[0015]The magnesium oxide thin film 2 is parenchyma top magnesium oxide, and impurities, such as oxidized silicon, a calcium oxide, and iron oxide, may be included two to 5% of the weight. The above-mentioned magnesium oxide thin film is easily hydroxide-ized with water vapor of not inertness but the air, and has become the mixed state with magnesium hydroxide seemingly. although a ratio of this oxide and hydroxide changes a little with a film formation condition and temporality -- about 40 atomic(s)% from analysis results, such as ESCA, -- although it is thought that it is contained, it has not clarified for details.

[0016]Thickness of this metal oxide thin film is obtained by calibration of a transmission electron microscope (TEM) and X-ray fluorescence analysis (XRF), and a thickness measurement method of this invention is based on the latter measuring method.

[0017]As a formation method of this metal oxide thin film, publicly known things, such as a vacuum deposition method, sputtering process, and the ion plating method, are possible. Especially, in a vacuum deposition method, what is called an electron beam heating method that carries out heating vacuum evaporation of the magnesium oxide material with an electron beam is required, and as this means, An electron beam generated with an electron gun provided in a publicly known vacuum chamber is deflected by a magnetic field, What is called a deviated type type with which an evaporation material is made to irradiate; a large-sized electron gun type made to irradiate with an electron beam generated with an electron gun which it had out of a vacuum chamber like the above, and which thing may be used, 3000-8000A/s high-speed evaporation is possible for the latter, and it can enlarge productivity.

[0018]The transparent primer layer 3 concerning this invention is formed between a metal oxide thin film and a 2 liquid hardening type urethane application layer, and giving stress relaxation to a thin film accompanying adhesive setting after pasting makes it the purpose. In particular, when a metal oxide thin film was comparatively as thin as 450-1500 A, an indispensable thing became clear as a result of inquiring wholeheartedly.

[0019]When thickness is 450A or less, by pasting, a crack will occur on a film by minute volume change by adhesive setting solvent attack etc., and oxygen interception nature after a layered product will deteriorate substantially as a result. When thickness is not less than 1500A, a crack will occur in a metal oxide thin film by bending etc., and oxygen interception nature will worsen.

[0020]Although a transparent primer layer in particular concerning this invention is not limited to the presentation for the above-mentioned Reason, it requires that a glass transition point should be not less than 40 **.

[0021]While an adhesives layer hardens so that it may mention later that a glass transition point is less than 40 **, this transparent primer layer will carry out a dimensional change, a crack generation of a metal oxide thin film will be caused for a Reason for the above, and barrier property after a layered product will deteriorate as a result.

[0022]On the other hand, if a glass transition point becomes not much high, the pliability of a coat will fall

and it will become a problem. Preferably, it is 40-80 **.

[0023]A polyvinyl chloride system, a polyvinyl chloride acetate copolymer system, a polyvinyl-butyril system, A polymethyl methacrylic system, a urethane system, a polyester system, a polyamide system, Heat-resistant thermosetting high polymer resin chosen from a nitrocellulose system, a cellulosic system, etc., such as thermoplastic polymer resin, a melamine system, and a urea system, can be used, may be used as a bridging body with a hardening agent if needed, and may be used.

[0024]Either, such as ultraviolet curing by which a glass transition point is represented with not less than 40 ** polyester acrylates, polyurethane acrylate, epoxy acrylate, polyethylacrylate, etc., and electron beam hardening resin, is used.

[0025]Although thickness in particular is not limited, it can be arbitrarily selected according to a kind of resin used at about 0.5-3 micrometers, and is not constant by the film hardness, elongation, pliability, etc. A uniform coat is not formed as it is 0.5 micrometer or less, and stress to a thin film is added by a volume change accompanying hardening of an adhesives layer, and degradation of a barrier is caused. It is efficiently unchanging although you may be not less than 3 micrometers.

[0026]Compared with a coat of an adhesives layer in this invention, this transparent primer layer of this invention has a high glass transition point, and it is desirable that they are a high strong (**) degree and low ductility. Although a thing of the same presentation as an adhesives layer is able to use for a transparent primer layer, compared with a glue line, a glass transition point is high and it is required to be a high hardness coat at low ductility.

[0027]Next, the 2 liquid hardening type urethane application layer 4 concerning this invention, Polyether polyurethane polyisocyanate which is main as for publicly known polyurethane adhesive, and has an isocyanate group at the end, A 1 liquid hardening type hardened at a reaction of polyester polyurethane polyisocyanate etc. and water which is sticking to moisture and a film surface in the air; a 2 liquid hardening type which forms a urethane bond and is hardened from base resin which has a hydroxyl group, and a hardening agent which has an isocyanate group is used for an end. Since the pliability of adhesives, hardness, elongation, etc. affect greatly oxygen interception nature degradation after a layered product, the optimal selection of a kind of a molecular weight of base resin, structure, and hardening agent is needed.

[0028]The printing layer 6 concerning this invention is what is formed on this transparent primer layer, A character and a pattern are formed with an ink paint film which adds various paints, an extender, stabilizer, etc. to ink binder resin used from the former, such as a urethane system, a polyamide system, acrylic, a nitrocellulose system, and a rubber system.

[0029]In the polyolefin resin layer 5 concerning this invention, 15-120-micrometer-thick polyethylene, They are polypropylene, an ethylene-vinylacetate copolymer, an ethylene-methacrylic acid copolymer, an ethylene-methacrylic-acid-ester copolymer, an ethylene-acrylic acid copolymer, ethylene-acrylic ester copolymers, those metal bridging body things, etc.

[0030]a method of laminating a thing of film state which consists of the above-mentioned resin as a method of laminating these resin layers by the publicly known dry laminate method and the non SORIRU vent laminating method -- further, Heat melting of the above-mentioned resin is carried out, and it can laminate by what is called method of carrying out an extrusion lamination that extrudes and laminates in curtain form, and a method with publicly known all.

[0031]A layered product of Claim 1 as mentioned above A metallic oxide, a transparent primer layer, The feature is in laminating one by one to a 2 liquid hardening type urethane system adhesives layer and a polyolefin layer, and also gas cutoff nature degradation after lamination is lost like Claim 2 by having passed composition in which a printing layer was formed on a transparent primer layer. When providing a printing layer additionally, even if it prints to a side which does not form a metal oxide thin film or laminates a printed substrate to the outermost layer, it is satisfactory at all.

[0032]

[Example]

The magnesium oxide thin film was continuously coated with the vacuum deposition by an electron beam heating method so that thickness might be 1000 Å at one side of the polyester film of 1> 12 micrometers of < working example thickness.

[0033]Base film: Substrate = biaxial-stretching polyethylene terephthalate film thickness =12micrometer width =500mm length =2000m [0034]Vacuum-evaporation conditions: Processing degree-of-vacuum

$=7 \times 10^{-4}$ (Torr)

Vapor rate = 5000A/s-electron gun condition = accelerating voltage 30kV-emission current 1A line speed = 60 m/min [0035] It was 980A when the magnesium oxide film thickness of the obtained deposition film was measured with X-ray fluorescence analysis. When the oxygen permeability of this film was measured by MOCON OXTRAN-10/50A made from MOCON, it was good at 2 ml/m² and day-atm (27 **).

[0036] Next, the usual 2 liquid hardening type urethane system adhesives for dry laminates after coating a transparent primer layer with polyester system resin were used for this deposition film, it pasted together to unextended polypropylene (CPP) 60micrometer, and the layered product was obtained.

[0037]

transparent primer layer: -- polyester polyol / tolylene DIISOSHIANETOADA Hardening layer of KUTO glass transition point [] -- 67 ** (based on the DSC method)

Mn⁽¹⁾ 3.29*10⁴/ 1.03*10³ Mw⁽¹⁾ 4.57*10⁴/ 1.52*10³ Mw -- ⁽¹⁾ / Mn⁽¹⁾ 1.39 / 1.48 thickness 1.5-micrometer*

notes: -- a ⁽¹⁾ polystyrene reduced property [0038] lamination condition: - lamination substrate: -- unextended polypropylene (cpp.60micrometer, Showa Denko make)

- Version : 180l. - 45 micro A gravure plate and adhesives : It is dilution base resin with a 2 liquid hardening type polyester urethane system / ethyl acetate. AD810A Hardening agent AD810B (made in Oriental Morton)

- Coating amount : 2.7 g/m² and drying temperature : 50-60-70 ** and nip conditions : 60 degree-3 kg/cm² and line speed: 30 m/min [0039] Thus, the obtained layered product was neglected for four days at 50 **, after hardening of adhesives, again, when oxygen permeability was measured, it was stable in 0.9 ml/m² and day-atm (27 **), and the good thing was obtained.

[0040] It was the same as that of <comparative example 1> working example 1, and without the transparent primer layer, it pasted together to CPP60micrometer by dry laminate directly, and the layered product was obtained.

[0041] It used for the <working example 2> transparent primer layer at 1.0 micrometer of saturated polyester resin (Ely Tell UE3210/Unitika) of 45 ** of glass transition points, and magnesium oxide pasted a 1000-A thing together to CPP60micrometer by dry laminate directly by survey, and obtained the layered product.

[0042] It was the same as that of <working example 3-4> working example 1, and magnesium oxide film thickness was 500 A and 700 A.

[0043] The ion bridge construction thing (ionomer resin: made in Mitsui E. I. du Pont de Nemours Pori Kem Cal) of an ethylene-methacrylic acid copolymer is extruded from a T die to curtain form on a polyester system transparent primer layer like <working example 5> working example 1, Line speed was adjusted so that thickness might be set to 30 micrometers, and the layered product was obtained.

[0044] Like the <comparative example 2> comparative example 1, without the transparent primer layer, extrusion coating of the ionomer resin was carried out directly, and the layered product was obtained.

[0045] It was the same as that of <comparative example 3> working example 1, and others obtained the layered product on the conditions using polyvinyl acetate resin whose glass transition point is 38 ** in the transparent primer layer.

[0046] A transparent primer layer is formed like <working example 6> working example 1, subsequently to this transparent primer layer top urethane system ink is used, and it is four colors, and is gravure printing ****. Subsequently, it laminated by CPP60micrometer and the dry laminate method on working example 1 and the conditions.

[0047] Ink: 1 liquid urethane system (made by LP gas super TOYO INK MFG. CO., LTD.)

**** : Sumi Red Yellow White [0048] Without the <comparative example 4> transparent primer layer, four color prints were carried out like working example 6 on the direct metal oxide thin film layer, and, subsequently the layered product was obtained by CPP60micrometer and the dry laminate method.

Hereafter, the evaluation result of working example is shown in Table 1.

[0049] It is the same as that of the <comparative example 5> comparative example 1 -- oxidation -- a mug - the thickness of NESHAMU was 3000 A.

[0050] 450 A of oxidized silicon was used for the <working example 7> metal oxide layer, and it laminated like working example 5.

[0051]It laminated like working example 6 without the <comparative example 6> transparent primer layer.

[0052]

[Table 1]

	金属酸化物 (膜厚 Å)	プライマー 層 (Tg)	酸素透過率(cc/m ² /day/atm)		評価
			積層前	積層後	
実施例 1	M g O (980 Å)	有 (67°C)	2.0	0.9	○
実施例 2	" (1000 Å)	有 (45°C)	1.9	0.8	○
比較例 1	" (1000 Å)	無	2.0	25.6	×
実施例 3	" (500 Å)	有 (67°C)	3.4	2.0	○
実施例 4	" (700 Å)	有 (67°C)	2.7	1.5	○
実施例 5	" (980 Å)	有 (67°C)	2.0	1.0	○
比較例 2	" (980 Å)	無	2.0	35.2	×
比較例 3	" (980 Å)	有 (38°C)	2.0	3 ~ 15	×
比較例 5	" (3000 Å)	無	0.5~10	0.3~5	×
実施例 6	" (980 Å)	有 (67°C)	2.0	1.3	○
比較例 4	" (980 Å)	無	2.0	16.8	×
実施例 7	S i O (450 Å)	有 (67°C)	1.8	1.3	○
比較例 6	" (450 Å)	無	1.8	15.6	×

[0053]

[Effect of the Invention]In laminating a glue line and a polyolefin resin layer one by one via the transparent primer layer excellent in dimensional stability on the metal oxide thin film provided on the transparent plastic film as mentioned above according to this invention. The practical layered product which the stress to this thin film layer by the minute volume change accompanying adhesive setting could ease by high elasticity and a low ductility transparent resin layer, could ease the stress accompanying the dimensional change to a metal oxide thin film eventually, and originally maintained the outstanding oxygen water steamy interception nature which a metal oxide thin film has is obtained.

[0054]

[Translation done.]